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(71) Applicant (for all designated States except US): DE SAN-GOSSE UK S.A. [FR/GB]; Market Weighton, P.O. Box 135, York Y04 3YY (GB).			
(72) Inventor; and		Published	
(73) Inventor/Applicant (for US only): BOWEN, Ivor [GB/GB]; 23 Maes Cadwgan, Creigiau, Cardiff CF4 8TQ (GB).		With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(74) Agent: BROWNE, Robin, Forsythe; Urquhart-Dykes & Lord, Tower House, Merthyr Vale, Leeds LS2 8PA (GB).			

(54) Title: MOLLUSCICIDES

(57) Abstract

A molluscicide containing a non-toxic animal repellent and metaldehyde, in which the molluscicidal efficacy of the molluscicide is greater than that of the molluscicide if it did not contain repellent. The repellent may be an anthranilate compound or d-pulegone which is present at a concentration of up to 1 %.

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Molluscicides

This invention relates to molluscicide formulations and in particular to molluscicide formulations for agricultural and horticultural purposes which act to repel non-targeted species while having an increased efficacy in killing a targeted species.

Prevention of damage to seeds and crops includes control of avian depredation and mammalian seed predators as well as consumption by mollusca. However, the ingestion of pesticides by non-targeted species can limit the use of such agricultural chemicals. To this end, a molluscicide formulation which concomitantly provides a non-toxic repellent to birds and mammals fulfils a need. Such a molluscicide formulation has advantages such as more specific targeting for a particular species, acting as a repellent to avert other species and being non-toxic to other species thereby reducing the hazard for non-targeted species.

According to a first aspect of the invention there is provided a molluscicide formulation containing a non-toxic animal repellent and metaldehyde. It has been found that combining a non-toxic animal repellent with metaldehyde in a molluscicide formulation has a synergistic effect on the efficacy of the molluscicide formulation; i.e. the molluscicide formulation kills a greater number of mollusca than if the molluscicide formulation did not contain the repellent. The animal repellent may be a bird and/or mammal repellent.

Such a molluscicide formulation has a number of advantages. It is more efficient at killing a targeted pest and so reduces damage to crops and seeds. It also helps to avert avian and mammalian pests from crops and seeds and so reduces damage by the pests. Further, as the repellent is non-toxic to avian and mammalian species it does not provide a hazard to them and so

-2-

may be employed as a pesticide in situations in which toxic repellents may not be used.

The repellent may be an anthranilate compound. Preferably the anthranilate compound is selected from methyl anthranilate, isobutyl anthranilate, ethyl anthranilate, isobutyl methyl anthranilate and dimethyl anthranilate. More preferably the repellent is methyl anthranilate or dimethyl anthranilate. Methyl anthranilate is a non-lethal bird repellent. Anthranilate derivatives are generally non-toxic. Methyl anthranilate is also biodegradable affording no detectable residues and therefore poses little environmental threat. Although methyl anthranilate is non-toxic, it has been found that at relatively low concentrations it acts synergistically with metaldehyde to improve molluscicidal efficacy as well as targeting and so may greatly enhance the environmental profile of molluscicides.

In preferred embodiments of the invention, the repellent is d-pulegone. This repellent is a potent non-toxic bird repellent and is used as a harmless mint flavouring in human foods. The compound is a non-phytotoxic terpenoid and comes from the pennyroyal plant (*Mentha pulegium*). It is used at concentrations greater than 1% in food preparations. Concentrations as low as 0.01% have been shown to repel birds significantly and the compound has also been shown to repel dogs. D-Pulegone has been found to perform at least as well as anthranilate compounds in terms of molluscicide synergy and to be better at lower concentrations. It is 10 times as efficient a bird repellent as dimethyl anthranilate and comparatively inexpensive leading to cheaper molluscicide formulations.

The repellent may be present at a concentration of not more than 1%. Preferably the repellent is present at a concentration of not more than 0.5%. Such low concentrations of repellent have been found to satisfactorily avert avian and mammalian pests and results in a cheaper molluscicide.

-3-

Percentages and amounts used in this specification are by weight unless indicated otherwise.

The metaldehyde may be present at a concentration of not more than 6%. The metaldehyde may be present at a concentration of not more than 4%. The metaldehyde may be present at a concentration of not more than 2%.

According to a second aspect of the invention there is provided use of a molluscicide formulation consisting essentially of a non-toxic animal repellant and metaldehyde.

The animal repellant may be selected from: methyl anthranilate, isobutyl anthranilate, ethyl anthranilate, isobutyl methyl anthranilate, dimethyl anthranilate and d-pulegone.

The repellant may be present at a concentration of not more than 1%, preferably not more than 0.5%.

The metaldehyde may be present at a concentration of not more than 6%, preferably not more than 4%, or more preferably not more than 2%.

According to a third aspect of the invention there is provided a molluscicide formulation comprising 92-96.5% flour, 6-2% metaldehyde, 1-0.5% non-toxic animal repellant and 1% calcium propionate

The invention is further described by means of example, but not in any limiting sense, with reference to the accompanying drawings, of which:

Figures 1-3 show a comparison of the mortality and grain loss rate in repellant and none repellant containing molluscicide formulations; and

-4-

Figure 4 shows a comparison of the efficacies of different amounts of metaldehyde in a repellent containing molluscicide formulation.

The synergistic advantage of combining a non-toxic bird and mammal repellent with a metaldehyde based molluscicide formulation has been demonstrated using a well established technique which simulates controlled field conditions.

Pellets were prepared by mixing Durum wheat flour with the following non-toxic repellents:

1. Methyl anthranilate (99.0% pure) BR1
2. Dimethyl anthranilate (95.0% pure) BR2
3. Methyl/Dimethyl Anthranilate (starch encapsulated at 19% w/w) BR3
4. D-Pulegone (95.0% pure) BR4

to give final concentrations of the repellents of 0.5% and 1%. Metaldehyde was added to the flour/repellent mixtures and thoroughly mixed to provide 2% and 4% metaldehyde w/w. The mixture was then compressed into small pellets having approximate dimensions of 5mm by 2mm. Similar pellets were made from metaldehyde and flour mixtures and flour only to provide control samples. The efficacy of the pellets was then tested in standardised terraria.

Test terraria in the form of trays measuring approximately 0.2m² had 100 wheat grains sown on a double thickness of filter paper as a test crop. Pellets were randomly added at the commercially recommended rate of approximately 200 g/100 m². Five pre-starved slugs within a narrow weight band were introduced per terrarium tray and two trays per category per replicate were used. This rate represents a heavy slug infestation of 400,000 per hectare in the field. A total of three replicates were undertaken at 17 °C. Using this technique the molluscicidal efficacy of 0.5% and 1% concentrations of the

Table 1: Mean data of three terraria trials showing slug mortality and grain loss.

		ALL FORMULATIONS CONTAIN 4.0% Metaldehyde														
		CONTROL	Blank	4.0% Metaldehyde	0.5% METHYL ANTHRANILATE	1.0% METHYL ANTHRANILATE	0.5% DIMETHYL ANTHRANILATE	1.0% DIMETHYL ANTHRANILATE	0.5% METHYL/DIMETHYL ANTHRANILATE	1.0% METHYL/DIMETHYL ANTHRANILATE	0.5% D-PULGOCINE	1.0% D-PULGOCINE	0.025% BITREX	0.050% BITREX	0.5% CINNAMAMIDE	1.0% CINNAMAMIDE
		DAY														
MORTALITY %	1	-	63.3	70.0	55.0	83.3	66.7	66.7	53.3	63.3	70.0	53.3	60.0	63.2	50.0	
	2	-	73.7	96.7	63.3	90.0	83.3	90.0	76.7	96.7	90.0	80.0	80.0	80.0	66.7	
	3	-	86.7	100.0	80.0	90.0	90.0	90.0	86.7	100.0	93.3	90.0	83.3	86.7	80.0	
	4	-	93.3	100.0	90.0	96.7	100.0	100.0	90.0	100.0	93.3	90.0	90.0	86.7	83.3	
	5	-	96.7	100.0	90.0	96.7	100.0	100.0	93.3	100.0	96.7	90.0	90.0	90.0	90.0	
	6	-	96.7	100.0	93.3	96.7	100.0	100.0	96.7	100.0	96.7	93.3	90.0	93.3	90.0	
	7	-	100.0	100.0	93.3	100.0	100.0	100.0	96.7	100.0	96.7	93.3	90.0	93.3	93.3	
GRAIN LOSS (%)	1	10.7	2.3	0.7	2.7	1.0	1.7	1.3	2.3	2.0	2.0	1.3	1.3	1.3	2.3	
	2	32.3	3.7	2.0	5.0	2.3	3.3	3.3	9.7	2.3	3.3	5.0	4.3	3.7	8.0	
	3	46.3	4.3	2.0	6.7	2.6	4.0	4.0	12.3	2.3	4.0	6.3	4.6	6.0	9.3	
	4	55.0	5.0	2.0	8.7	3.0	4.3	4.3	16.0	2.3	4.0	7.3	4.6	6.7	9.7	
	5	56.7	5.0	2.3	8.7	3.0	4.3	4.3	17.0	2.3	4.0	9.0	4.6	7.0	9.7	
	6	64.0	5.0	2.3	8.7	3.3	4.3	4.3	17.0	2.3	4.3	9.0	4.6	7.0	9.7	
	7	69.7	5.0	2.3	8.7	3.3	4.3	4.3	17.0	2.3	4.3	9.3	5.0	7.0	10.3	
NON-VIABLE GRAINS (%)		3.0	7.6	7.0	5.3	3.3	2.7	4.3	0.7	2.7	3.0	0.3	2.3	5.7	5.7	
MICROBIAL INFECTION (%)		1.0	1.0	0.3	0.7	1.3	0.7	1.0	0.7	-	0.3	0.7	-	1.0	2.0	

-6-

different repellents in a 4% metaldehyde molluscicide formulation was investigated by comparison with flour and metaldehyde pellets and flour pellets.

The results obtained using 4% metaldehyde as the molluscicide are summarized in Table 1. The mean data represent the results of three terraria trials and demonstrate % slug mortality and % grain loss obtained using different bird repellent additives. A certain amount of grain loss is recorded representing un-germinated or non-viable grains. The relative performance of bird repellents against each other and the control pellets is shown in Figures 1 to 3.

As can be seen the anthranilate and d-pulegone compounds enhance the molluscicidal efficacy at the concentrations added compared to the metaldehyde alone pellets. Methyl anthranilate is more efficacious at a concentration of 0.5% than at 1% and most of the repellents were more efficient at the lower concentration of 0.5%. The best performance was recorded for d-pulegone which achieved a 100% mortality rate at a concentration of 0.5% in 4% metaldehyde by the third day of exposure. D-Pulegone performed slightly better than methyl anthranilate (MA) when used at the 1% level. The repellents dimethyl anthranilate (DMA) and a starch encapsulated mixture of MA/DMA were found to closely follow D-pulegone and MA in terms of improved molluscicidal efficacy.

A comparison of the efficacy obtained at 2% metaldehyde and 4% metaldehyde using a 1% concentration of bird repellent additive was carried out using a similar experimental technique as before. Figure 4 shows that overall 4% metaldehyde formulations are the most efficacious with d-pulegone and methyl anthranilate showing the greatest synergistic effect. Formulations containing 6% metaldehyde by weight are also envisaged.

-7-

Other animal repellent compounds such as Bitrex and Cinnamamide were not found to enhance the molluscicidal efficacy over that of the 4% metaldehyde alone formulation at the concentrations used.

-8-

CLAIMS:

1. A molluscicide formulation containing a non-toxic animal repellant and metaldehyde.
2. A formulation as claimed in claim 1, in which the animal repellant is a bird and/or mammal repellant.
3. A formulation as claimed in claim 1 or claim 2, in which the repellant is an anthranilate compound.
4. A formulation as claimed in claim 3, in which the repellant is selected from: methyl anthranilate, isobutyl anthranilate, ethyl anthranilate, isobutyl methyl anthranilate and dimethyl anthranilate.
5. A formulation as claimed in claim 2, in which the repellant is methyl anthranilate.
6. A formulation as claimed in claim 2, in which the repellant is dimethyl anthranilate.
7. A formulation as claimed in claim 1 or claim 2, in which the repellant is d-pulegone.
8. A formulation as claimed in any preceding claim, in which the repellant is present at a concentration of not more than 1%.
9. A formulation as claimed in any preceding claim, in which the repellant is present at a concentration of not more than 0.5%.
10. A formulation as claimed in any preceding claim, in which the metaldehyde is present at a concentration of not more than 6%.

-9-

11. A formulation as claimed in any preceding claim, in which the metaldehyde is present at a concentration of not more than 4%.

12. A formulation as claimed in any preceding claim, in which the metaldehyde is present at a concentration of not more than 2%.

13. A method of use of a molluscicide formulation comprising a non-toxic animal repellant and metaldehyde.

14. A method as claimed in claim 13, in which the animal repellant is selected from: methyl anthranilate, isobutyl anthranilate, ethyl anthranilate, isobutyl methyl anthranilate, dimethyl anthranilate and d-pulegone.

15. A method as claimed in claim 14, in which the repellant is present at a concentration of not more than 1 %.

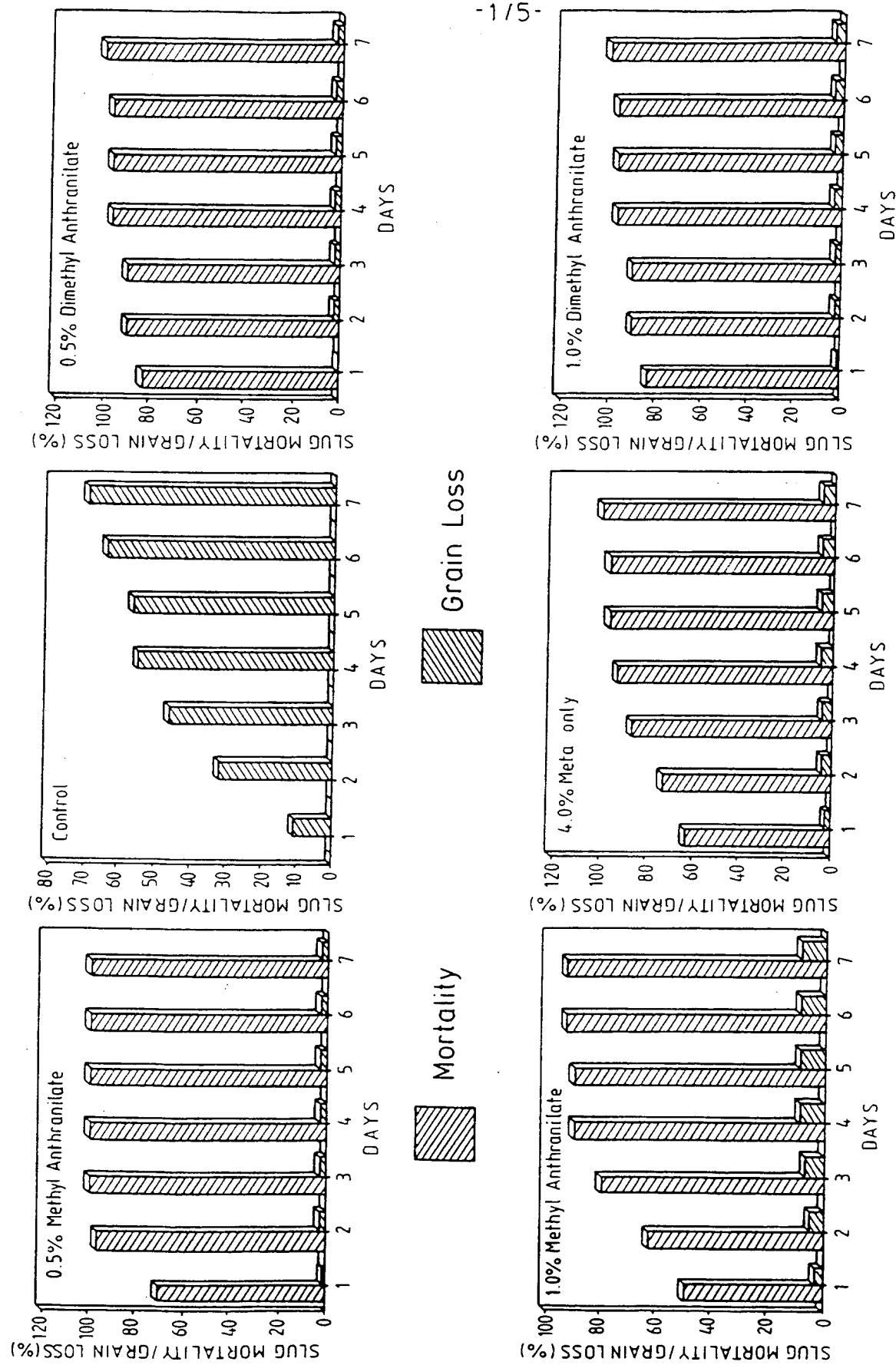
16. A method as claimed in claim 14, in which the repellant is present at a concentration of not more than 0.5%.

17. A method as claimed in any of claims 13-16, in which the metaldehyde is present at a concentration of not more than 6%.

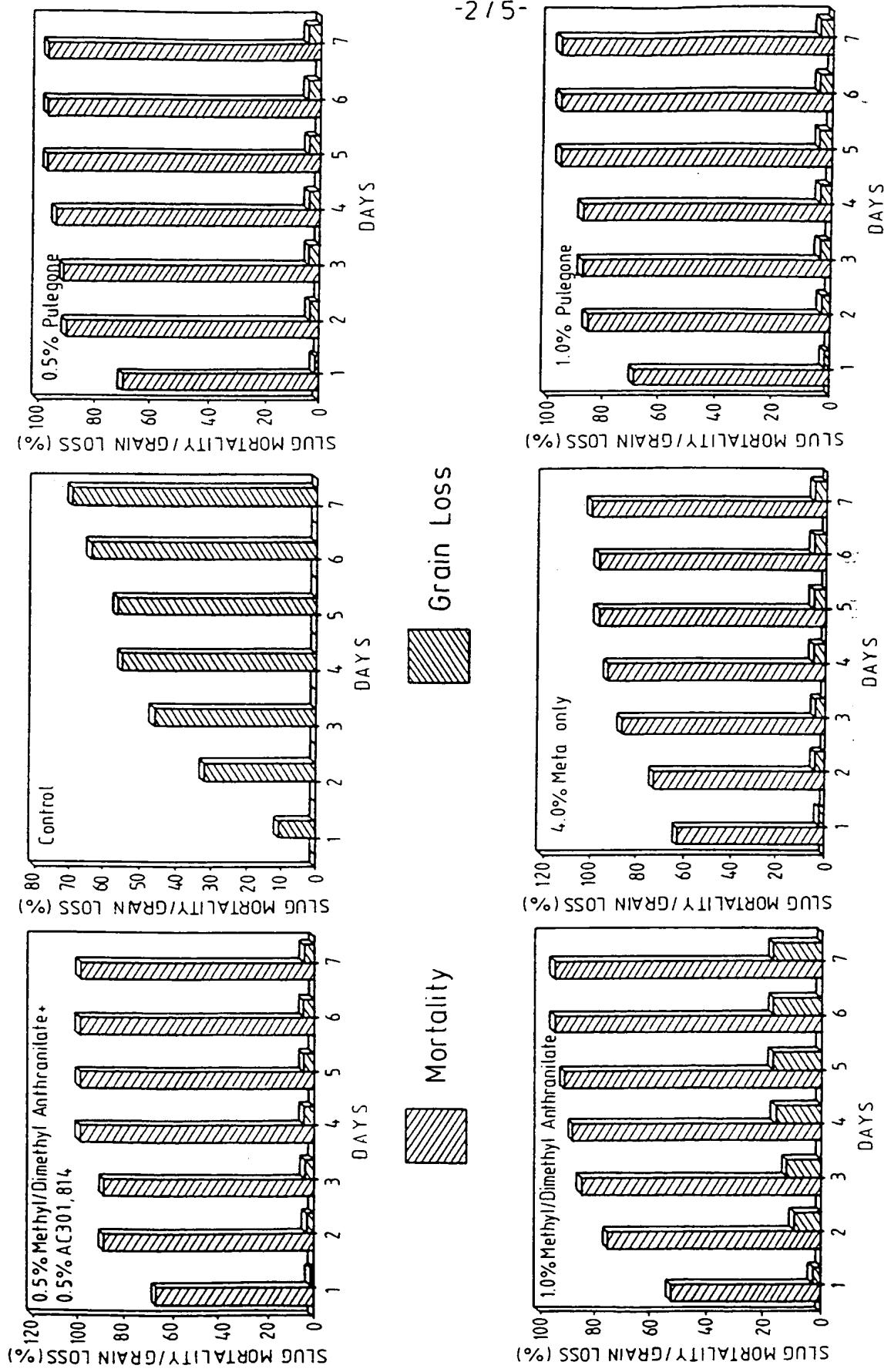
18. A method as claimed in any of claims 13-16, in which the metaldehyde is present at a concentration of not more than 4%.

19. A method as claimed in any of claims 13-16, in which the metaldehyde is present at a concentration of not more than 2%.

20. A molluscicide formulation consisting of 92-96.5% flour, 6-2% metaldehyde, 1-0.5% non-toxic repellant and 1% calcium propionate.



-215-



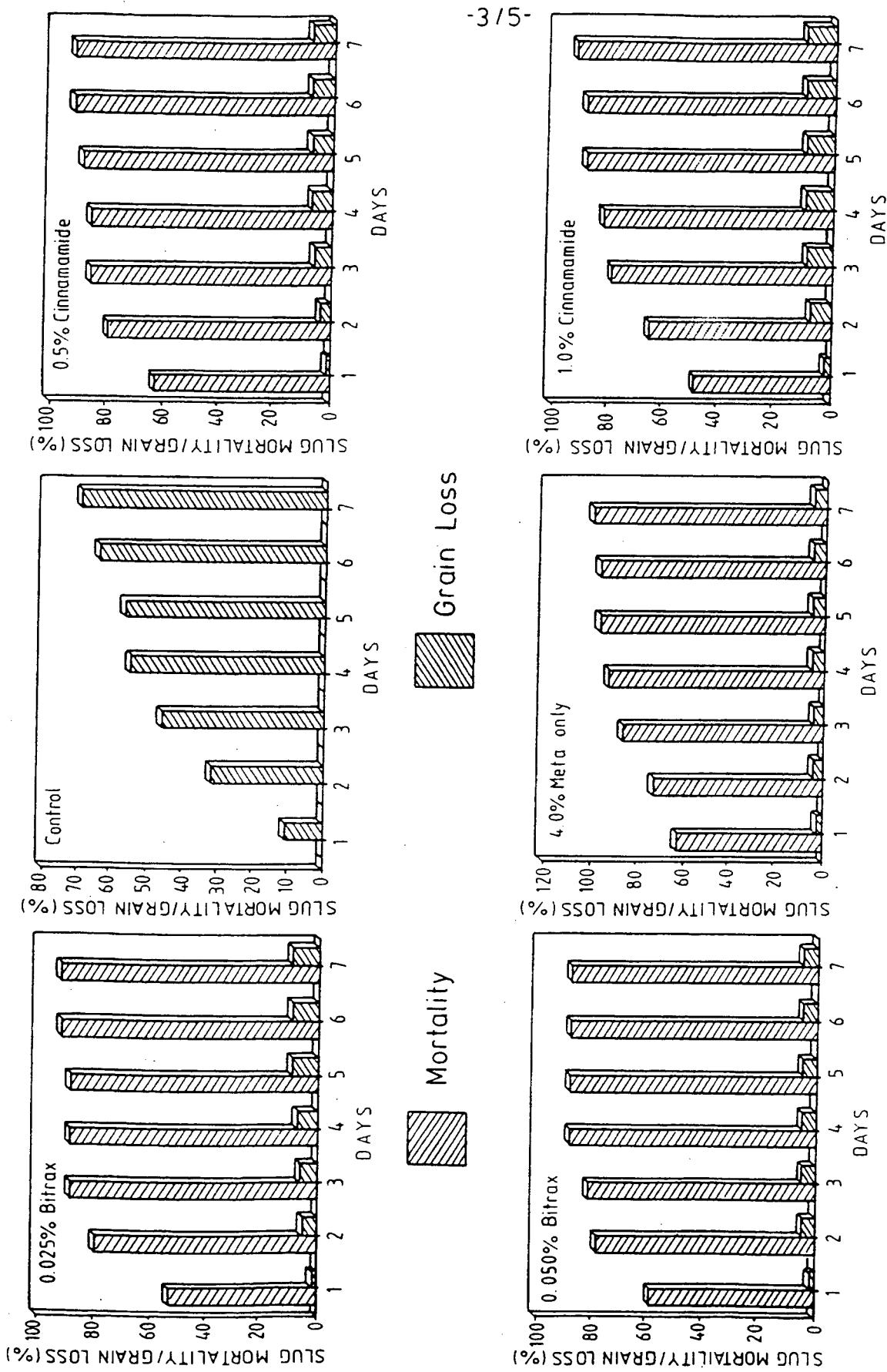
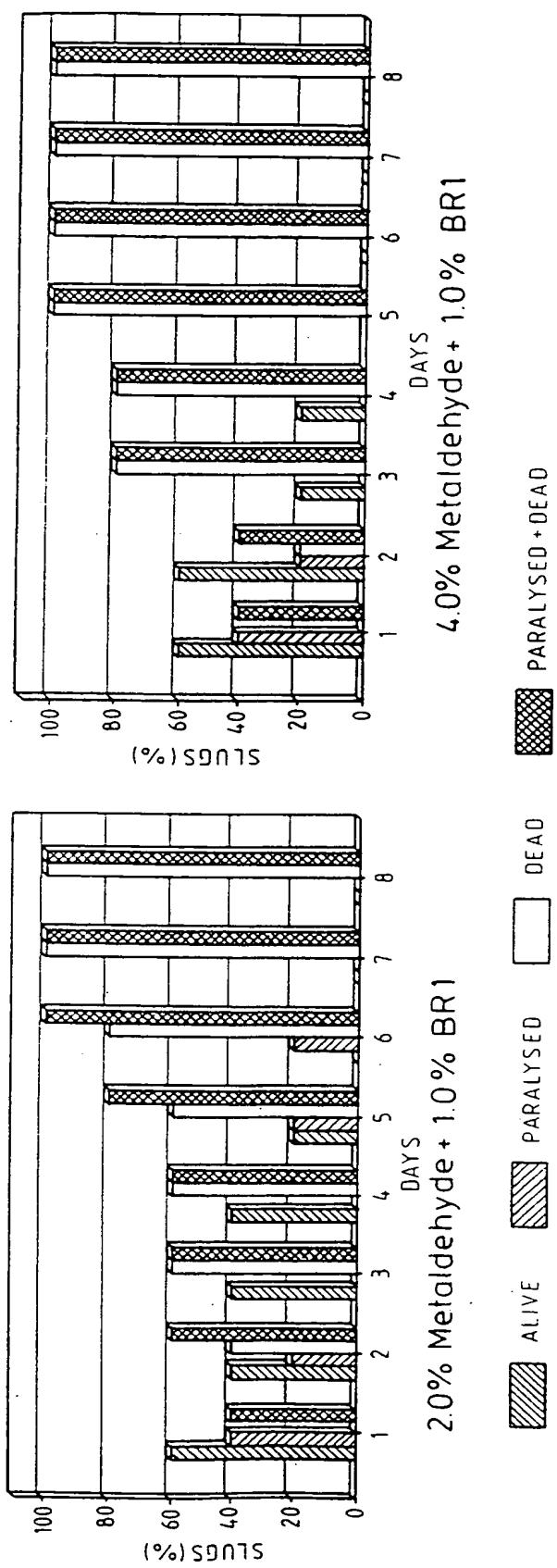
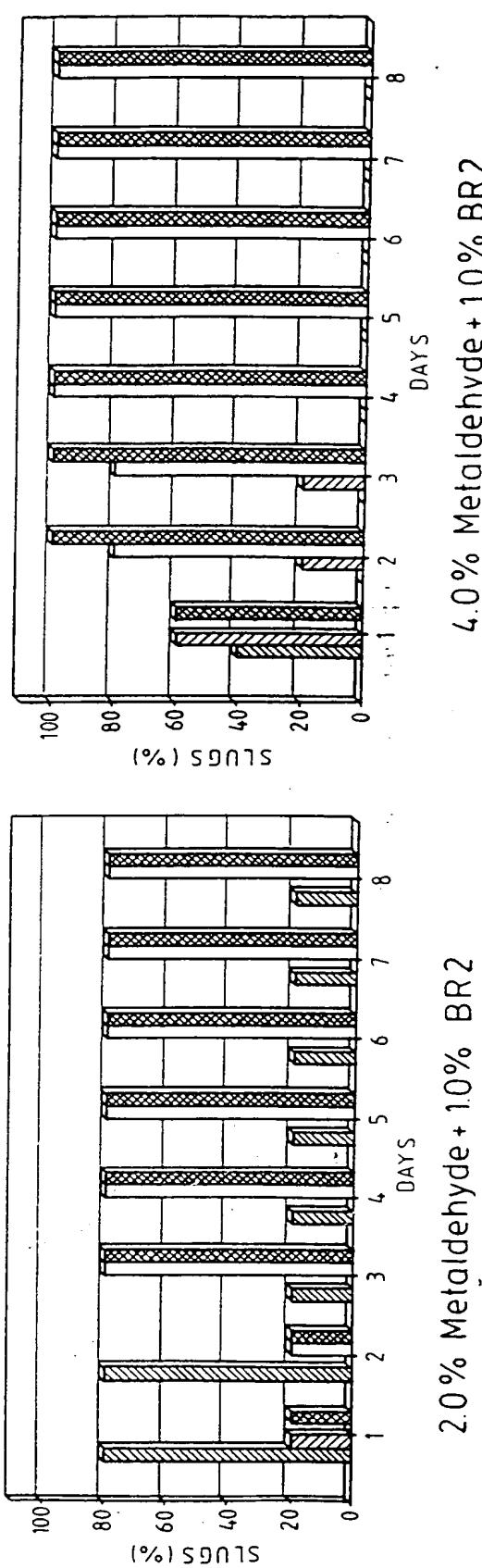


FIG. 3

-415-



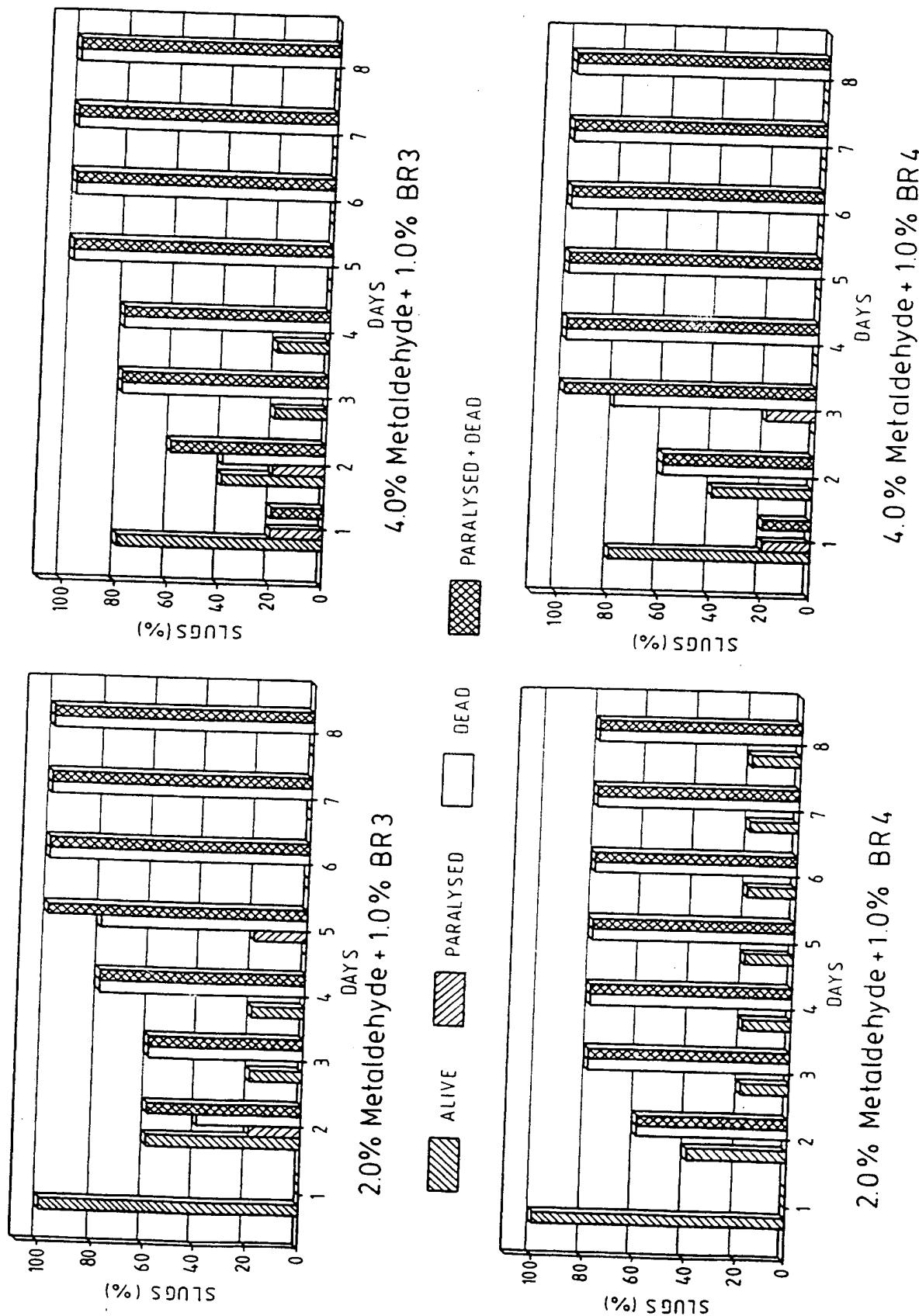
4.0% Metaldehyde + 1.0% BR1



2.0% Metaldehyde + 1.0% BR2

FIG. 4

-5/5-



INTERNATIONAL SEARCH REPORT

Int	tional Application No
PCT/GB 98/01258	

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N35/02 A01N25/00 // (A01N35/02, 37:44, 35:06)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 314 846 A (R & C PRODUCTS PTY LTD) 10 May 1989	1, 2, 8-13, 17-19
Y	see page 2, line 11 - line 51 see page 4, line 13 - line 44; claims 1-5, 10 ----- -/-	3-7, 14-16, 20

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Muellners, W

INTERNATIONAL SEARCH REPORT

 Int'l Application No
 PCT/GB 98/01258

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 122, no. 17, 24 April 1995 Columbus, Ohio, US; abstract no. 207728, MASTROTA, F. NICHOLAS ET AL: "Evaluation of taste repellents with northern bobwhites for deterring ingestion of granular pesticides." XP002077132 see abstract & ENVIRON. TOXICOL. CHEM. (1995), 14(4), 631-8 CODEN: ETOCDK; ISSN: 0730-7268, 1995, ---	3-5, 7, 14-16
Y	US 2 967 128 A (M.R. KARE) 3 January 1961 see column 1, line 15 - line 61 see column 6, line 11 - line 19; claims 1, 3 ---	6
Y	US 4 581 378 A (LAZAR REMUS ET AL) 8 April 1986 see column 2, line 23 - line 25 see column 3, line 57 - line 59 ---	20
A	US 4 765 979 A (NIELSEN JAMES W) 23 August 1988 see column 1 - column 4, line 21 and the example ---	1-20
A	US 3 090 723 A (S.A PASTAC) 21 May 1963 see column 1 - column 2, line 49 ---	1-20
A	CHEMICAL ABSTRACTS, vol. 118, no. 21, 24 May 1993 Columbus, Ohio, US; abstract no. 207529, NOLTE, DALE L. ET AL: "Avoidance of bird repellents by mice (Mus musculus)" XP002077133 see abstract & J. CHEM. ECOL. (1993), 19(3), 427-32 CODEN: JCECD8; ISSN: 0098-0331, 1993, ---	3-6, 14
A, P	CHEMICAL ABSTRACTS, vol. 126, no. 25, 23 June 1997 Columbus, Ohio, US; abstract no. 326877, WAGER-PAGE, SHIRLEY A. ET AL: "d-pulegone: a feeding deterrent to deer mice (Peromyscus maniculatus) and prairie voles (Microtus ochrogaster)" XP002077134 see abstract & CHEMOECOLOGY (1996), 7(3), 146-149 CODEN: CHMOE9; ISSN: 0937-7409, 1996, -----	7, 14
A		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01258

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0314846 A	10-05-1989	CH 673931 A FR 2598286 A PT 84842 B US 4940583 A	30-04-1990 13-11-1987 08-02-1990 10-07-1990
US 2967128 A	03-01-1961	NONE	
US 4581378 A	08-04-1986	AU 9178682 A BR 8300468 A CA 1186988 A GB 2114443 A, B IN 158810 A JP 58150501 A	18-08-1983 01-11-1983 14-05-1985 24-08-1983 31-01-1987 07-09-1983
US 4765979 A	23-08-1988	NONE	
US 3090723 A	21-05-1963	NONE	

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